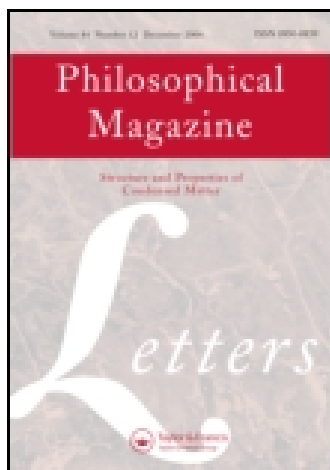


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$\text{Nd}_2\text{O}_3 : \text{Eu}^{3+}$ nanocrystalline phosphor-a new potential thermoluminescing material for dosimetry

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Nd₂O₃:Eu³⁺ nanocrystalline phosphor – a new potential thermoluminescing material for dosimetry

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Nanoparticles of trivalent Eu³⁺-doped Nd₂O₃ phosphors have been prepared using a low-temperature solution combustion method with metal nitrate as precursor and oxalyldihydrazide as a fuel at a fairly low temperature (<500°C) and in a very short time (<5 min). A powder X-ray diffraction pattern reveals that cubic Nd₂O₃:Eu³⁺ crystallites are directly obtained without the requirement of further calcinations. The crystallite size, evaluated from Scherer's formula, was found to be in the range of 20–30 nm. The microstructure and morphology were studied by scanning electron microscopy, which showed the phosphor to be foamy and fluffy in nature. Thermoluminescence characteristics of the Nd₂O₃:Eu³⁺ have been studied using gamma irradiation. These demonstrate that the phosphor is suitable for use as a dosimeter.

Keywords: nanocrystalline material; dosimetry; chemical synthesis; luminescence

1. Introduction

Following the advent of nanotechnology, there is a considerable amount of research involved in the search for new crystalline phosphor materials with good thermoluminescence (TL) properties. The most widely developed application of such materials is their use in radiation dosimetry [1], which spans areas of health physics and other biological sciences, radiation protection and personal monitoring [2]. TL is a very sensitive probe in order to detect defects in concentrations of the order of 10⁷ cm⁻³. Soliman [3] has reported that commercial Nd₂O₃ is an efficient

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gamma-ray dosimeter. To the best of our knowledge, there have been only a few reports [4,5] on the synthesis of Nd_2O_3 phosphor by polyol and sol-gel auto combustion methods. Furthermore, we are unaware of any attempt at the synthesis of Nd_2O_3 using low-solution combustion (LSC) synthesis. In this article, we report on the LSC synthesis of $\text{Nd}_2\text{O}_3 : \text{Eu}^{3+}$ phosphors using metal nitrates and oxalyldihydrazide (ODH) fuel. The prepared phosphors have been well characterized using different spectroscopic techniques such as powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) and TL, the results of which are discussed.

2. Experimental

2.1. Synthesis of $\text{Nd}_2\text{O}_3 : \text{Eu}^{3+}$ nanocrystalline phosphors

An aqueous solution containing stoichiometric amounts of analar grade neodymium nitrite, europium nitrate and ODH was contained in a petri dish of approximately 300 mL capacity. The excess water was allowed to evaporate during heating over a hot plate until a wet powder was left. Then the dish was introduced into a muffle furnace maintained at $400 \pm 10^\circ\text{C}$. The reaction mixture underwent thermal dehydration and ignition at one spot with the liberation of gaseous products such as oxides of nitrogen and carbon. The combustion propagated throughout the reaction mixture without further need of any external heating, as the heat of the reaction was sufficient for the decomposition of the redox mixture. The flame temperature was measured using an optical pyrometer and was found to be $1400 \pm 100^\circ\text{C}$, which persists for a few seconds. Finally, a voluminous and porous product was obtained.

2.2. Instruments used

The phase purity and crystallinity of the phosphor has been examined by PXRD with a Philips X-ray diffractometer model PW 3710 using $\text{Cu-K}\alpha$ radiation and a nickel filter. The size, shape and distribution of the grains were examined using a JEOL (JSM-840A) SEM. FT-IR studies of the sample were performed on a Perkin-Elmer FTIR spectrometer (Spectrum 1000). The TL measurements were made using a Nucleonix TLD reader. Details of the experimental setup have been described elsewhere [6].

3. Results and discussion

Figure 1 shows the PXRD pattern of the as-formed $\text{Nd}_2\text{O}_3 : \text{Eu}^{3+}$ (0.1 mol%). The pattern was compared with JCPDS card no. 21-0579 and found to match perfectly with the standard data and a pure cubic phase. When crystallites are less than approximately 100 nm in size, appreciable broadening in the X-ray diffraction lines occurs. The observed line broadening can be used to estimate the average grain size.

Assuming that the particles are stress-free, the size can be estimated from a single diffraction peak by Scherrer's method using silicon as the internal standard [7]. The average grain size of crystallites d is given by

$$d = \frac{0.89\lambda}{\beta \cos \theta}, \quad (1)$$

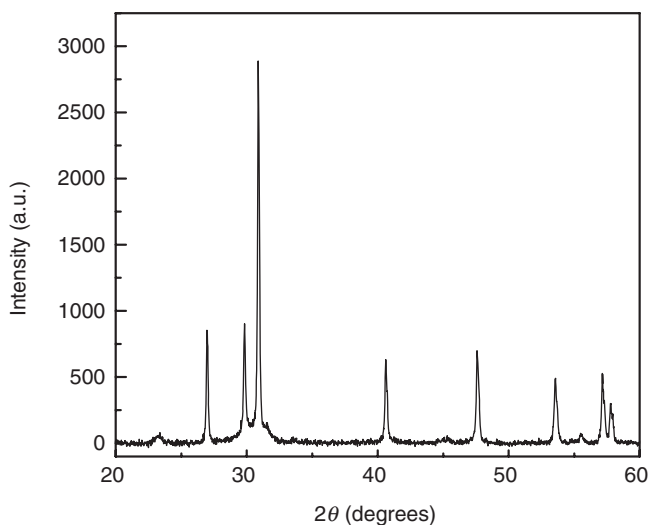


Figure 1. PXRD of Eu (0.1 mol%)-doped Nd_2O_3 phosphor.

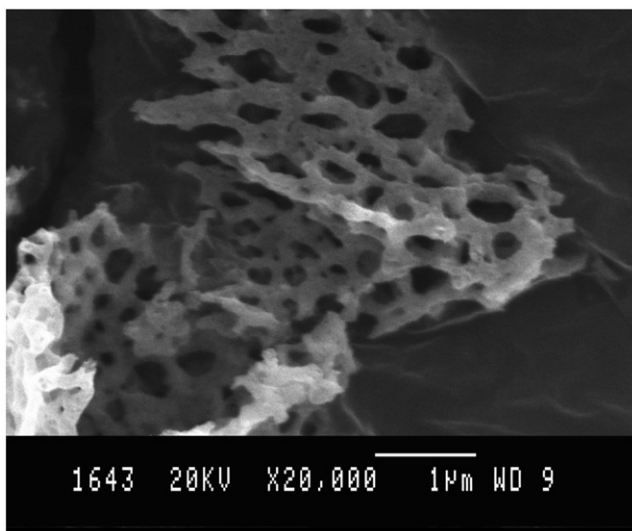


Figure 2. SEM image of Eu (0.1 mol%)-doped Nd_2O_3 phosphor.

where λ is the incident wavelength, θ the Bragg angle and β the full-width at half-maximum (in radians) of the diffraction peak. The grain size of the presently studied phosphor was calculated to be approximately 20–30 nm.

The surface morphological features of the Eu (0.1 mol%)-doped Nd_2O_3 phosphor is shown in Figure 2. The phosphor shows pores, and voids with cage-like structure composed of very fine polycrystalline circular nanoparticles. The porous nature can be attributed to the large amount of gas escaping from the reaction mixture during combustion [8].

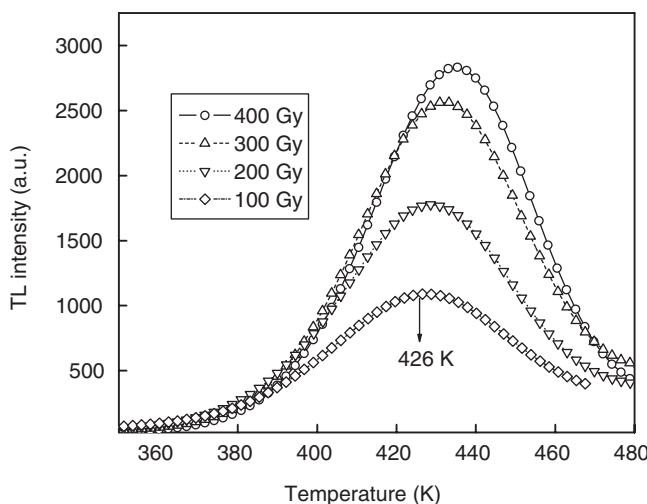


Figure 3. TL glow curves of $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystalline phosphor.

The characteristic FTIR spectrum of 0.1 mol% Eu-doped neodymium oxide exhibits broad and strong peaks at 2820 and 3396 cm^{-1} corresponding to the stretching mode of $-\text{OH}$ from the water crystallization. The strong peaks at 1597 cm^{-1} and 1452 cm^{-1} represent the asymmetric and symmetric stretch of $\text{O}-\text{C}-\text{O}$, respectively [5]. The peak at 1134 cm^{-1} is due to $\text{C}-\text{OH}$ bonds, and the peaks at 878 and 846 cm^{-1} are due to $\text{C}-\text{H}$ bonds. The weak peak at 709 cm^{-1} is associated with the metal-oxygen $\text{M}-\text{O}$ bond.

One of the most desirable properties of a TL dosimeter is that it should exhibit a linear relationship between TL intensity and absorbed dose. Figure 3 shows the TL glow curves of $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ (0.1 mol%), with a γ -irradiated dose of 100–400 Gy. A well-resolved glow peak at $\sim 426\text{ K}$ was recorded at a heating rate of 5°C s^{-1} . It is seen that, up to a given dose, the form of the glow curve and its peak position remain unaffected. To the best of our knowledge, the application of synthesized $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ as a dosimeter is a new concept which has not yet been studied in detail. The dose response of γ -irradiated samples was investigated by plotting the TL intensity as a function of irradiation dose (Figure 4). The TL intensity of the samples follows a linear relation with increasing dose between 100 and 400 Gy. Initially, the creation of trapping centers is small for low doses. For higher doses the creation of trapping centers is greater and, as a result, the TL intensity increases.

The effect of different heating rates on the TL glow peaks of $\text{Nd}_2\text{O}_3:\text{Eu}$ was studied between 10 and 100°C s^{-1} (in steps of 10°C s^{-1}). With increase in the heating rate, the peak intensity, as well as the total area of the peaks, decreases and the peak temperature shifts to a higher temperature. The shift in the glow-peak temperature with heating rate can be easily understood. At a low heating rate β_1 , the time spent by the phosphor at a temperature T_1 is sufficiently long that a thermal release of electrons, depending on the half-life at this temperature, takes place. As the heating rate increases from β_1 to β_2 , the time spent at the same temperature T_1 decreases, and, therefore, the thermal release of electrons is also decreased. So at a higher

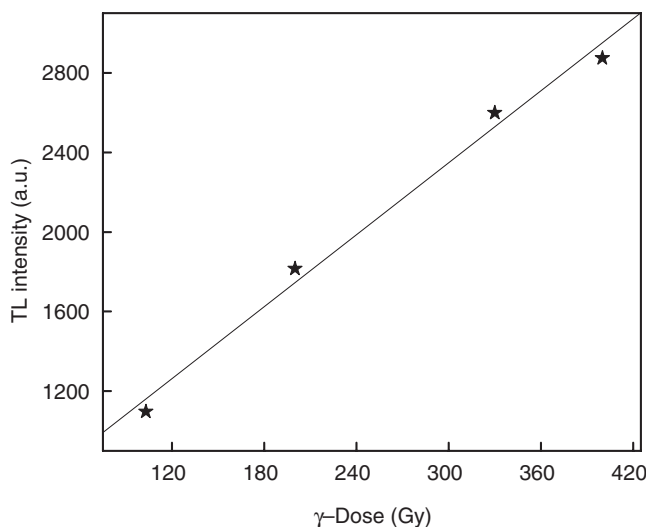


Figure 4. Variation of glow peak intensity as a function of irradiation dose.

temperature T_2 , the same amount of thermal release is required to take place at β_2 . In this way, the whole glow curve and hence the glow peak temperature increases with the heating rate in a manner depending on the half-life and the time spent at each temperature. Similar results were observed by Gorbics et al. [9]. These authors observed a decrease of both integral area and the peak TL intensity versus heating rate, and assigned it to thermal quenching whose efficiency increases as the temperature increases. Therefore, since the glow peak shifts to higher temperatures, it suffers from thermal quenching.

Fading is the unintentional loss of the TL signal. It leads to an underestimation of the absorbed dose. Fading may be due to several causes. Thermal fading originates from the fact that even at room temperature there is a certain probability of charge carriers escaping from their trapping centers. Fading may also be caused by optical stimulation. In general, high-sensitivity materials should be handled carefully and stored in opaque containers to prevent fading from light exposure. Other types of fading, which are not temperature dependent, are caused by quantum mechanical tunneling of the trapped charge to recombination sites and transitions between localized states, i.e. transitions that do not take place via the delocalized bands [10].

Initially, the high fading effect of gamma-irradiated samples is due to the recombination of the trapped electrons released at room temperature. After initial fading the sample becomes stable, and new recombination can occur only by heating the sample at elevated temperatures. To study the fading effect, the phosphor $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ (0.1mol%) was given a test dose of 200 Gy from a gamma source (Co^{60}) and the TL signal was recorded at different intervals for nearly 21 days. Figure 5 shows the plot of TL intensity versus the number of days after exposure. Strong fading was observed initially after four days; the decay is quite slow and finally stabilizes after 21 days. This is due to an increase in the energy barrier in the nanocrystalline phosphor; at lower doses the concentration of defect creation

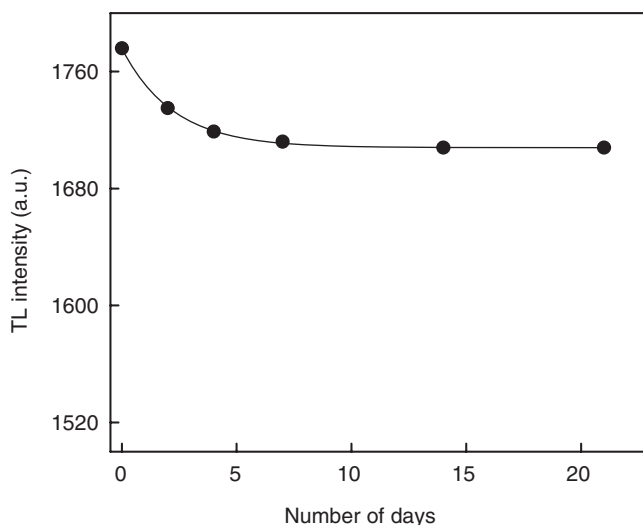


Figure 5. TL fading of $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ (0.1 mol%) exposed to 200 Gy of gamma irradiation for a period of 21 days.

is minimal. The cause of fading at low doses is possibly due to the formation of shallow and thermally unstable traps [11]. However, it is further speculated that on irradiating the nanocrystalline phosphor at high doses, deeper traps are formed, as a result of which the fading will be less.

Pallavi et al. [11] have studied TL properties of β -irradiated $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Tb}^{3+}$ (1%). The fading effect of the phosphor was measured by giving the sample a test dose of 100 Gy from a Sr-90 beta source. The TL signal was recorded at different intervals for nearly two months. Strong fading was observed after 10 days of irradiation with the phosphor losing around 59% of the TL signal. After this time, the decay was quite slow and finally stabilized after 30 days. The 41% remnant TL signal is high enough to be considered for dosimetric applications. Rodriguez et al. [12] have studied TL of nanocrystalline and single crystals of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) exposed to beta irradiation. To characterize the fading, both nanocrystalline and single-crystal phosphors were irradiated with beta rays for 300 Gy, and the TL signal was measured at different times after irradiation. For the nanocrystalline YAG, strong fading was observed after 12 h with the TL signal losing around 75% of its initial value. Subsequently, the signal decayed slowly and finally stabilized after 48 h. The 25% remnant signal is high enough for dosimetry. For the YAG crystal, strong fading occurred in the first 56 h with the signal stabilizing after 194 h having been reduced to 65%. The 35% remnant signal can be considered for dosimetric applications. In the present study, the fading is less (<30%) and so this phosphor might also have potential use in dosimetry.

If the sensitivity of a phosphor does not change after several cycles of exposure and readouts, then this is obviously desirable for dosimetric applications. The phosphor $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ (0.1 mol%) has been tested for this reusability. The sample was exposed to a gamma dose of 100 Gy and the TL glow curve recorded at the same heating rate (5°C s^{-1}) as before. It was then quickly cooled to room temperature and

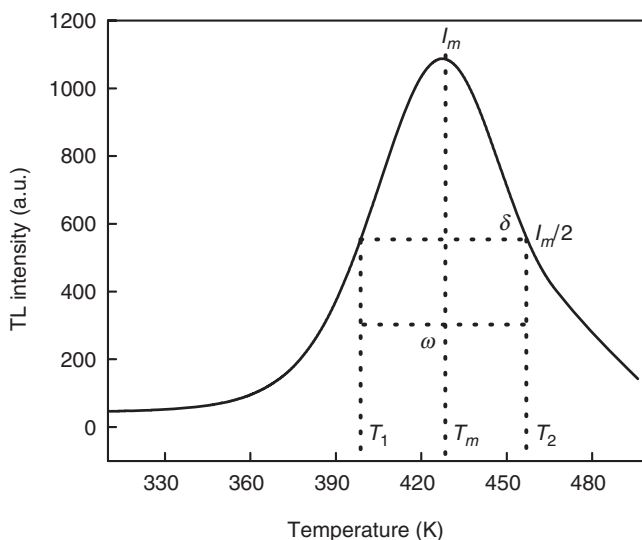


Figure 6. Representative diagram of different quantities used in the glow-curve shape method.

again exposed to 100 Gy in order to accumulate the dose. The glow curve was recorded for the second time. Four such cycles were performed, during which it was observed that only marginal variations in the intensity of the 426 K peak occurred.

The trap parameters, such as activation energy E , order of kinetics b , were calculated for the 426 K glow peak of the $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ (0.1 mol%) nanocrystalline phosphor irradiated with a gamma dose of 100 Gy at room temperature using the Chen's set of empirical formulae [13] for the shape of the glow curve. The activation energy and order of kinetics can be estimated using the following relations:

$$E\alpha = c_\alpha \left(\frac{kT_m^2}{\alpha} \right) - b_\alpha (2kT_m) \quad (2)$$

$$\alpha = \tau, \delta, \omega \quad \tau = T_m - T_1 \quad \delta = T_2 - T_m \quad \omega = T_2 - T_1$$

$$C_\tau = 1.51 + 3.0(\mu_g - 0.42) \quad (3)$$

$$C_\delta = 0.976 + 7.3(\mu_g - 0.42) \quad (4)$$

$$C_\omega = 2.52 + 10.2(\mu_g - 0.42) \quad (5)$$

$$b_\tau = 1.58 + 4.2(\mu_g - 0.42), \quad b_\delta = 0, \quad b_\omega = 1$$

$$\mu_g = \frac{T_2 - T_m}{T_2 - T_1}. \quad (6)$$

The nature of the kinetics can be found by the form factor. A representative diagram of different quantities used in the glow-curve shape method while determining the trap parameters is shown in Figure 6. Theoretically, a value of the geometrical form factor μ_g , which is close to 0.42, implies first-order kinetics, and

a value of 0.52 is for second-order processes. In the present study, a value very close to 0.42 was found, suggesting first-order kinetics. The average activation energy was found to be 1.03 eV. Soliman [3] has studied the TL characteristics of Nd_2O_3 powder procured from Sigma Aldrich. He observed three glow peaks in the range of 310–385°C in the as-received samples. However, in the case of calcined sample, four glow peaks were observed in the range of 170–385°C at a dose of 600 Gy. In the present study, a single well-resolved glow peak at 426 K was observed in $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ samples. The variation in glow-peak temperature and the number of glow peaks in $\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystalline phosphor relative to bulk phosphor could arise from nanosize effects, namely particle size and the increased surface-to-volume ratio [14]. It may also be noted that the TL glow peak temperature and intensity depend on various parameters including the nature of the sample (crystalline, semi-crystalline, non-crystalline), the history of the sample (pre-exposed to natural radiations, age of the sample, etc.), the impurity content, the heat treatment given to the sample prior to irradiation, the nature of ionizing radiation, the amount of irradiation (dose/fluence), temperature at which the TL measurements are made, the time interval between measurements, the environment of the sample during experiment (humidity, atmospheric gas etc.), the type of detector and the heating rate.

4. Conclusions

$\text{Nd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystalline phosphors have been prepared at a low temperature (400°C) and in a very short time (<5 min). PXRD pattern showed the presence of a cubic phase. SEM studies showed the presence of porous and fluffy in nature with agglomerated nanoparticles. The study of TL characteristics shows that the phosphor exhibits good linearity, low fading and reusability. Therefore, up to a given irradiation dose, this phosphor has potential for use in radiation dosimetry.

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